Local sources identification of trace metals in urban/industrial mixed land-use areas with daily PM10 limit value exceedances

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Abstract

This study presents the analysis of the concentration levels, inter-site variation and source identification of trace metals at three urban/industrial mixed land-use sites of the Cantabria region (northern Spain), where local air quality plans were recently approved because the number of exceedances of the daily PM10 limit value according to the Directive 2008/50/EC had been relatively high in the last decade (more than 35 instances per year). PM10 samples were collected for over three years at the Torrelavega (TORR) and Los Corrales (CORR) sites and for over two years at the Camargo (GUAR) site and analysed for the presence of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), titanium (Ti), vanadium (V), molybdenum (Mo), manganese (Mn), iron (Fe), antimony (Sb) and zinc (Zn). Analysis of enrichment factors revealed an anthropogenic origin of most of the studied elements; Zn, Cd, Mo, Pb and Cu were the most enriched elements at the three sites, with Fe and V as the least enriched elements. Positive Matrix Factorisation (PMF) and pollutant roses (Cu at TORR, Zn at CORR and Mn at GUAR) were used to identify the local sources of the studied metals. Analysis of PMF results revealed the main sources of trace metals at each site as road traffic at the TORR site, iron foundry and casting industry at the CORR site and a ferro-manganese alloys industry at the GUAR site. Other sources were also identified at these sites, but with much lower contributions, such as minor industrial sources, combustion and traffic mixed with the previous sources.

Keywords: Trace elements, Source identification, Positive matrix factorization, Inter-site variation

1. INTRODUCTION

The levels of PM10 (suspended particulate matter with an aerodynamic diameter of less than 10 μm) in some European urban and industrial areas usually exceed the yearly and daily limit values of 40 and 50 $\mu g/m^3$, respectively, set by the European Air Quality Directive 2008/50/EC (Querol et al., 2008; Putaud et al, 2010; European Environmental Agency, 2012).

Cantabria is a small coastal region located in northern Spain, where the number of exceedances of the daily PM10 limit value in some urban-industrial mixed land-use areas was higher than the maximum number of exceedances allowed by Directive 2008/50/EC (35 instances per year). This Directive states that air quality plans should be developed for zones and agglomerations in which the pollutant concentrations in ambient air systematically exceed the air quality target/limit values. These air quality plans must incorporate, at least, information related to the origin of the pollution, including the main emission sources, the total quantity of emissions from point sources, and information on pollution from long-range sources. Table 1 shows the number of exceedances of the daily PM10 limit value at the monitoring stations of Cantabria from 2003 to 2011. According to the exceedances primarily found at the Los Corrales de Buelna, Camargo and Torrelavega (Barreda) sites from 2003 to 2008, three local air quality plans were developed in the Cantabria region (Consejería de Medio Ambiente, Ordenación del Territorio y Urbanismo del Gobierno de Cantabria, 2007; 2012a;2012b).

The measured mass of PM depends on many sources that are not located near the receptor sites, such as secondary inorganic and organic aerosols and other long-range sources (Lewandowska and Falkowska, 2013; Skyllakoul et al., 2014), sea-salt aerosol (Arruti et al., 2011a; Lewandowska and Falkowska, 2013) and some crustal sources (Salvador et al., 2013). However, the emission of particles from local sources increases the levels of PM10 and micropollutants, such as trace metals and some organic compounds (Dongarrà et al., 2007); the main local anthropogenic sources can be mobile (from vehicles) or stationary (residential and industrial combustion and other industrial activities). Considering the number of daily PM10 exceedances at the Cantabria sites (Table 1), a high contribution from local sources to the PM10 levels at the sites of Camargo, Torrelavega (Barreda site) and Los Corrales de Buelna may be anticipated, because the number of daily PM10 exceedances at the other sites in the Cantabrian Air Quality Network is relatively low.

Trace metals are good tracers of local industrial emissions (Moreno et al., 2006); thus, the source apportionment of metals in urban areas that are influenced by local industrial activities can be incorporated into such air quality plans to help reduce the PM10 levels and their associated toxicity. Two main groups of source apportionment techniques are usually reported in the literature (Viana et al., 2008). The first group consists of source-receptor modeling by means of deterministic models. From a mathematical point of view, this approach is highly complex and requires reliable emission datasets from inventories or direct measurements of pollutants to model the dispersion, transformation, transport and deposition of such contaminants (Maes et al., 2009). The second group of models is based on the statistical evaluation of the pollutants measured at receptor sites. Receptor modeling has been widely applied in source apportionment studies in different environmental matrices, such as rainwater (Junto and Paatero, 1994), bulk deposition (Huston et al., 2012; Fernández-Olmo et al., 2014) and PM10 (Polissar et al., 1998; Almeida et al., 2006; Alleman et al., 2010). Some recent reviews in the literature have addressed the use of receptor models with PM data (Reff et al., 2007; Viana et al., 2008). Major components, trace metals, and organic compounds are usually considered in these analyses. Chemical Mass Balance (CMB), Principal Component Analysis (PCA) and Positive Matrix Factorisation (PMF) are the most commonly used techniques (Viana et al., 2008). PMF was developed by Paatero and Tapper (1994) as an alternative to other factor analysis techniques. The major improvement of this technique is that it forces all the values in the solution profiles and factor contributions to be non-negative, which is more realistic than their treatment in PCA. PMF was first applied to precipitation data (Junto and Paatero, 1994) and bulk wet deposition samples (Anttila et al., 1995) with the aim of identifying the most important sources of ions and major elements. Later, PMF was extensively applied to PM10 data for the apportionment of metals and major components (Reff et al., 2007; Alleman et al., 2010).

Additionally, methods based on the evaluation of monitoring data, for example, correlating meteorological variables, such as wind direction with levels of air pollutants, have also been used (Eilers, 1991; Somerville et al., 1996), sometimes in combination with receptor modelling (Yue et al., 2008; Alleman et al., 2010; Chan et al., 2011). The relationship between the levels of single pollutants and the wind direction is usually reported by means of pollutant concentration roses, which are polar diagrams that depict how air pollution depends on wind direction (Eilers, 1991). If an ambient air quality monitoring station is markedly

influenced by the source of a measured pollutant, the corresponding pollutant concentration rose will contain a peak towards the local source (Cosemans and Kretzschmar, 2002). In this work, three urban-industrial mixed land-use areas located in the Cantabria region of northern Spain, where local air quality plans have been established due to the number of exceedances of the daily PM10 value, were selected to study the levels of trace metals and local sources. Trace metals are considered good tracers of local sources and have therefore been chosen in this study to assess the contribution of local anthropogenic activities by using one of the most commonly employed receptor modelling techniques, Positive Matrix Factorisation (PMF).

2. MATERIALS AND METHODS

2.1. Study area

Three areas of the Cantabria region, a small coastal area located in northern Spain, which have recently had local air quality plans approved due to daily PM10 level exceedances were studied in this work:

1) In the southern part of Santander Bay, an urban station, Camargo, registered a high number of daily PM10 limit value exceedances (Table 1). PM10 filters were sampled at another station, Guarnizo (GUAR, 43º24'12" N, 3º50'36" W, 11 m.a.s.l.), which is located close to the Camargo station (approximately 1 km SW) and may be considered an urban/industrial site. The vicinity of Camargo is an important industrial area for iron, steel and ferromanganese alloys manufacturing.

2) An urban/industrial station named CORR (43º15'48" N, 4º03'51" W, 89 m.a.s.l.) is located in the town of Los Corrales de Buelna. This site had a high number of daily PM10 exceedances, mainly between 2003 and 2007 (Table 1). Industrial activities related to drawing and iron foundry and casting are located in the southern and eastern parts of the town.

3) In the town of Torrelavega, a monitoring station named Barreda (TORR, 43º21'43" N, 4º02'47" W, 13 m.a.s.l.) also registered a high number of daily PM10 exceedances (Table 1). TORR is an urban background site, but is also influenced by traffic and industrial sources. The main industrial activities in this area include pulp and paper, and chemical plants with intensive fossil fuel use.

As shown in Figure 1, the distance between the monitoring sites is short, and a circle with a radius of 12 km encompasses the three sampling points.

2.2. Sampling and analysis

PM10 sampling was carried out in 2008 and 2009 at the GUAR site and in 2008, 2009 and 2010 at the TORR and CORR sites. Because the PM10 filters were collected within the framework of the three local air quality plans, the sampling was carried out by the local government and the number of filters, the duration of the sampling campaign and the amount of air volume filtered for each sample were fixed by the technical staff of the local environmental authorities. Thus, low volume samplers (2.3 m^3/h) were used to collect 48 h samples on quartz micro-fibre filters (47 mm diameter, Sartorius) in 2008 and 2009, and 24 h samples were used in 2010. According to Directive 2004/107/EC, a minimum of 14 % time coverage was used for the studied years.

The analysis of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), titanium (Ti), antimony (Sb), vanadium (V) and zinc (Zn) in the PM10 samples was conducted in accordance with the standard UNE-EN 14902:2006 (standard method for the measurements of Pb, Cd, As, and Ni in the PM10 fraction of suspended particulate matter). Each filter was digested using a mix of HNO_3 and H_2O_2 in a microwave digestion system (ETHOS). The digested samples were analysed by inductively coupled plasma mass spectrometry (ICP-MS) on an Agilent 7500 CE with a collision/reaction cell operating in hydrogen mode to avoid matrix interferences. Quality control of the analytical procedure was performed by evaluating the recovery values of the analysed pollutants in a standard reference material (SRM 1649a "urban dust"). The blank contribution from the filters and reagents were evaluated and subtracted from the results. The element recovery obtained from SRM1649a, the average of the filter blanks and the method detection limits (MDLs) are shown in Table 2. Further details about the analytical methodology can be found in Arruti et al. (2010; 2011a).

The hourly wind data required to calculate the pollutant and wind roses were available at the CORR and GUAR sites. At the TORR site, the meteorological station was located 1 km SW. The meteorological and major pollutant data were supplied by the Cantabrian Air Quality

Monitoring Network. The pollutant roses were calculated from the hourly wind direction data and 48 h metal concentration data using the procedure given in Cosemans and Kretzschmar (2002). The computed pollutant concentration rose is a vector with a dimension equal to the number of sectors used, in this case 36.

$$c_i = \sum_{j=1,n} p_j \cdot f_{i,j} \cdot \alpha_j \Big/ \sum_{j=1,n} f_{i,j} \cdot \alpha_j \quad (1)$$

where:

j: day index for the period under investigation.
n: the number of days in the period for which the rose is constructed.
i: the wind sector index for the rose. Range of 1-36 for sectors of 10º.
c_i: the resulting average concentration for wind sector *i* in all the studied period.
p_j: the measured concentration on day *j*.
$f_{i,j:}$ the number of hours that the wind came from sector *i* on day *j*.
α_j: a weight function based on the persistence of the wind vector during day *j*.

In this case, α_j is set to the inverse of the number of wind direction bins on day *j* with non-zero frequency, n_j.

$$\alpha_j = 1/n_j \quad (2)$$

2.3. Source apportionment

A comprehensive discussion of the theoretical basis of PMF can be found in the literature (Paatero and Tapper, 1994; Reff et al., 2007; Hopke, 2009). Briefly, PMF solves the receptor modelling equation (see equation 3), where the input ambient data matrix (e.g., concentration of metals bound to PM) equals the product of two new matrices, the factor profile (F) and the contribution of each source (G) plus a residual matrix (E). Thus, in matrix form,

$$X = GF + E \quad (3)$$

which can also be written in index notation as

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}, \quad \text{where} \quad i \in [1,n]; j \in [1,m]; k \in [1,p] \quad (4)$$

where *n* is the number of samples and *m* is the number of species. The coefficients of F and G are calculated for a given number of factors (*p*). This is an optimisation problem in which the objective function to be minimised is a modified error matrix (Q), which takes into account the uncertainties of each measured pollutant in each sample (σ_{ij}) with the constraints that each of the coefficients of the G and F matrices is to be non-negative (Hopke, 2000).

$$Q = \sum_{i=1}^{n} \sum_{j=1}^{m} \left[\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{\sigma_{ij}} \right]^2 \quad (5)$$

The global minimum of Q calculated from equation (5) is compared with the minimum value of Q ($Q_{theoretical}$) obtained from equation (6):

$$Q_{theoretical} = nm - (n+m)p \quad (6)$$

The uncertainties of the metal concentrations below the MDL were calculated as 5/6 MDL and as $4\overline{x_{ij}}$ for the identified outliers. For data that was greater than the MDL, the uncertainties were calculated according to equation (7):

$$\sigma_{ij} = (MDL_j^2 + (d_j x_{ij})^2)^{1/2} \quad (7)$$

which was first used by Anttila et al. (1995) for bulk deposition samples. Equation (7) is also proposed by the EPA PMF 3.0 software (US EPA, 2008), where d_j is the error fraction calculated from the geometric average of the relative standard deviation (RSD) for each metal, which is the instrumental error associated with the measurements. Any experimental value below the MDL was replaced by half of the MDL, and the geometric mean was used in place of missing data and identified outliers.

With respect to the number of factors, three factors led to the best combination of Q values and significance test results (p-value). A total of 100 random runs were used to ensure that local minima were not obtained. F_{peak}=0 was used in the developed models because the rotation of factors from assigning different values of F_{peak} did not improve the model performance.

The following criteria were considered to select the best models: comparison between the predicted and observed data through the time series, the parity plots, the significance test (p-

value), the difference between the calculated Q and $Q_{theoretical}$ and the physical meaning of the factor profiles.

3. RESULTS AND DISCUSSION

3.1. Levels of trace elements

The mean, standard deviation, maximum, minimum and median values of the concentrations of the studied trace elements are shown in Tables 3, 4 and 5 for the TORR, CORR and GUAR sites, respectively. Some of the studied elements are regulated by the European Air Quality Directives (As, Cd, Ni and Pb) and the annual limit/target values are given for these elements. Additionally, Mn and V are also included in the guidelines of the World Health Organization (WHO). These target/limit/guideline values are summarized in Table 6.

Tables 3, 4 and 5 show that the annual mean levels of the metals regulated by the EU (As, Cd, Ni and Pb) do not exceed the EU annual limit/target values (6, 5, 20 and 500 ng/m^3, respectively) at any of the sites. However, some individual samples at the CORR site exceeded the annual target value for Ni (i.e., 20 ng/m^3): a maximum 48 h value of 52.1 ng/m^3 was detected in 2008, but the annual mean values (4.5, 3.27, and 3.48 ng/m^3 in 2008, 2009 and 2010, respectively) were well below the annual target value. The levels of V at the three sites were well below the recommended WHO guideline (1000 ng/m^3 on a 24 h basis); however, the annual guideline value for Mn given in the WHO guidelines (150 ng/m^3) was exceeded at the GUAR site in 2008. Moreover, maximum 48 h Mn values of 515 and 587 ng/m^3 were found in 2008 and 2009, respectively. Manganese concentrations may increase to an annual average of 200–300 ng/m^3 in the proximity of foundries and to over 500 ng/m^3 in the presence of ferromanganese alloys industries (Howe et al., 2004). The GUAR site is located 1 km SW of a plant that produces ferromanganese and silicomanganese alloys.

The levels of the studied metals were graphically compared with values that are typically observed at Spanish urban and mixed land-use sites (Querol et al., 2007) in Figure 2. Additionally, Table 7 summarizes the mean metal concentrations detected in different Spanish and European urban and urban/industrial mixed land-use areas. With the exception of Mn, Fe and Zn, the levels of the studied metals at the CORR, TORR and GUAR sites are lower than those observed in other Spanish and European cities. High levels of Mn and Zn were present

in Llodio (Spain) and Dunkerque (France), which can be explained by the presence of iron and steel industries in these areas (Moreno et al., 2006; Gaudry et al., 2008). Concerning Spanish urban areas, higher concentration levels of Mn and Zn relative to the range detected in Spain can be clearly observed in Figure 2, mainly at the TORR and CORR sites for Zn and the GUAR site for Mn. The levels of the remaining studied elements were within the range, or even below the range, of those found in other Spanish urban areas.

At the TORR site, the highest metal concentrations were observed for Zn, Cu, Mn and Cr (see Figure 2a). Although TORR is an urban/traffic mixed site, the level of Cu, a road traffic tracer, is lower than that found at other urban/traffic sites, such as Palermo, Rome and Athens, and industrial sites, such as Llodio, Tarragona and Huelva (see Table 7). The levels of Zn, Cu and Mn were similar in the studied period. However, the Cr level at this site in 2008 was clearly higher than the level in other Spanish cities, whereas its level decreased significantly in 2009 and 2010;. this was attributed to the decrease in coal combustion in the industrial facilities located near the TORR sampling point due to the economic crisis. A strong influence of the economic crisis on the levels of trace metals associated with industrial activities was observed in the first semester of 2009 in the Cantabria region in a previous study (Arruti el al., 2011b). Zinc and Mn had the highest concentration levels at the CORR and GUAR sites. The local industrial activities (iron foundries at CORR and a ferromanganese alloys plant at GUAR) may explain the high values obtained for both elements. This will be discussed further in Source apportionment section.

3.2. Inter-site variation

Considering the relative proximity of the three sampling sites (see Figure 1), an inter-site analysis was performed to determine whether common or local sources affected the levels of trace metals at the studied sites. For this purpose, two techniques were used: the coefficient of divergence (COD) and the inter-site Pearson correlation coefficient for each trace element (Wilson et al., 2005). For these calculations, only samples collected simultaneously were considered. The COD provides information about the degree of uniformity between two sampling sites for a different number of pollutants as seen in equation (8) (Wongphatarakul et al., 1998):

$$COD_{jk} = \sqrt{1/n \sum_{i=1}^{n} ((x_{ij} - x_{ik})/(x_{ij} + x_{ik}))^2} \quad (8)$$

where x_{ij} represents the average concentration for a trace element *i* at sites *j* and *k*, and *n* is the number of trace elements. Small inter-site COD values are obtained for sites with common sources, whereas COD values approaching unity indicate great differences (i.e., different local sources at each site). According to previous studies, sites with COD values greater than 0.2 are influenced by different types of sources (Wilson et al., 2005). Table 8 shows the inter-site COD values for the studied period, which ranged from 0.22 to 0.37, suggesting that the three sampling sites are influenced by a combination of sources. The smallest COD value was obtained between the CORR and TORR sites (0.22) in 2009; in general, the lowest COD values were calculated for 2009, when the economic crisis was stronger in Cantabria (Arruti et al., 2011b). The decrease in COD in 2009 is attributed to the reduction in local industrial activities while the common sources (mainly road traffic and domestic combustion) were maintained.

Additionally, inter-site Pearson correlation coefficients were applied for each studied element, as shown in Table 9. The highest correlations were found for Ti, V and Mo. Titanium is typically found in resuspended urban soil, V is a tracer of combustion, and Mo is good tracer of road traffic (Arruti et al., 2011a). However, Mn, a local industrial marker at the GUAR site due to its proximity to a ferromanganese alloy plant, had low inter-site Pearson correlation coefficients for TORR-GUAR and CORR-GUAR, indicating that the origin of Mn at the CORR and TORR sites is not the ferromanganese alloy plant.

The sampling sites were also compared by analysing the enrichment factors of the trace elements (EF). The procedure was based on the standardization of the measured element with respect to a reference element and is shown in equation (9). Reference elements are usually characterized by low occurrence variability, and the most commonly used elements are Al, Ti and Fe. In this study, Ti was selected as a reference because of its relative natural abundance, its even distribution in the crust and the relatively low influence of anthropogenic activities on its observed levels. The reference environmental matrix was the earth's crust and the reference values were obtained from Li et al (2009).

$$EF_i = (X_i/Ti)_{sample}/(X_i/Ti)_{crust} \quad (9)$$

In these calculations, $X_{i,sample}$ and $X_{i,crust}$ are the concentration in air and the average concentration in the crust of element *i*. The EF values were calculated for all the studied elements, with the exception of Sb (its crustal concentration was not available), at the three sites and are shown in Figure 3. According to the EF values, the elements can be considered highly enriched (EF>100), intermediately enriched (10<EF<100) and less enriched (EF<10) (Berg et al. 1994). Iron was the least enriched element, followed by V and Mn at the CORR and TORR sites. Although the level of Mn at the three sites was higher than the corresponding range found in the Spanish urban areas (Figure 2), this element is considered highly enriched only at the GUAR site. Figure 3 also shows that the most enriched elements were Zn, Cd, Mo, Pb and Cu at the three sites. Chromium was also highly enriched at the TORR site in 2008, but became intermediately enriched in 2009 and 2010, due to the significant decrease in the concentration in air after 2008. Comparison of the EF values at the three sites indicates that Cu and Mo, which are typically tracers of road traffic, were more enriched at the TORR site, presumably due to the greater impact of road traffic at the TORR site with respect to CORR and GUAR.

3.3. Source apportionment

Three factors were selected to solve the PMF models, which were able to associate more than 89% of the metals analysed in the PM10 samples from the three receptor sites. Figures 4, 5 and 6 show the source profiles obtained from the PMF analysis of the TORR, CORR and GUAR sites, respectively. Chromium was excluded from the PMF analysis because the MDL was high and the Cr level in many samples was below its MDL. The percentages of each species among the factors are shown by square symbols (right y-axis), and the contribution of each species to the concentration for each factor is given in bar charts (left y-axis). The factors were sorted according to the amount of the metal concentration explained by the model. The contributions of each factor at the three sites are shown in Table 10.

At the TORR site, Cu is the main tracer of Factor 1, followed by Fe, Sb and Mo. The contribution of the first factor was approximately 55 %, which is attributed to road traffic. A significant correlation between these four elements and NO_x was observed at this site. Although industrial and domestic combustion contribute to total NO_x emissions, road traffic is their major source. The highest correlations between NO_x and the studied elements were

obtained for Fe > Mo > Sb > Cu. Copper and Sb are usually associated with the wear of vehicle brakes (Thorpe and Harrison, 2008). In particular, Cu and Sb were well correlated with organic carbon at the TORR site in a previous work (Moreno, 2010), and the author attributed this to the local traffic around the sampling site. In addition, Mo was well correlated with typical traffic markers, such as NO_x and the particle count in a roadside environment (Harrison et al., 2003) and total carbon (Arruti et al., 2011a). The origin of traffic-related Mo has remained unclear in the literature. Molybdenum can be found in engine lubricants as MoS_2 (Spada et al., 2012), and incorporated into road dust through oil leakage, but it can also be found in exhaust gases from oil combustion. Sjödin et al. (2010) calculated metal emission factors from road traffic in Sweden and estimated that 24 % of Mo is emitted in exhaust gases, 56 % is due to brake wear and 14 % is due to tyre wear.

The second factor is mainly composed of Pb, Cd, As and Zn and is attributed to local industrial activities. In particular, a Zn sulphide ore roasting plant is located 4 km NNE of the sampling site. Zinc had the highest correlation between SO_2 and the studied elements. Lead, As, Cd and Fe are the typical impurities found in Zn sulphide ores. Zinc and Fe had the highest mass contribution to factor 2, although both metals were distributed among the three factors. Finally, V and Ni, which are typically associated to combustion of liquid fuels, were the main tracers of the third factor. No significant correlations were observed between Ni and the major pollutants monitored at the TORR site; V was only well correlated with PM10. The influence of the meteorological conditions on the levels of the studied elements was assessed by analysing the wind patterns during the studied period and building and plotting pollutant roses. The wind rose for the TORR site was constructed for the period 2008-2010 and is shown in Figure 7 (a). The prevailing wind direction is WSW, following the direction of the Besaya River towards the sea. A small contribution from the NE sector is also shown in Figure 7(a), corresponding to moderate onshore breezes, mainly present in the summer. Because Cu was the main tracer of the first factor, it was used to compute a pollutant rose calculated from hourly wind direction data and 48 h Cu concentration data using the procedure described in the experimental section. Plotting the pollutant roses on local maps may help to identify the local sources of any metal. Figure 8 shows the Cu rose plotted on the TORR site area. Although the wind rose clearly indicated a prevailing WSW direction, the Cu rose is homogeneously distributed, which agrees with a traffic contribution from all sectors around the sampling site because some motorways and main roads are located nearby.

Although three local industrial plants are located to the W/SW direction of the sampling site, as shown in Figure 8, the levels of Cu do not appear to be affected by these local plants.

At the the CORR site, the first factor explains more than 73 % of the metal contribution, showing high levels of Zn, Mn and Fe. This factor is associated with the local iron foundry and casting plants, which use iron and steel scrap and pig iron as starting materials and some ferromanganese alloys as alloying additions. Steel scrap usually contains high amounts of Zn. The second factor is mainly composed of Pb, Cd, Cu and Sb. The concentration of Zn and Fe in this factor remains noticeable. The composition of this factor is attributed to a mixed contribution from traffic and local industry because Cu and Sb are usually identified as traffic tracers and a local wire drawing plant that contains Zn and Pb baths is located approximately 750 m SE of the sampling site (see A3 in Figure 9). Finally, the third factor is associated with V and Ni and is attributed to liquid fuel combustion. At the CORR site, most of the studied elements were well correlated with PM10 and NO_x, and only Ni did not have any significant correlation with the major pollutants.

The wind rose calculated for the CORR site in 2008-2010 is shown in Figure 7(b). The wind pattern at this site is clearly different than that found at the other sites, with a high contribution from the S, SSE, N and NW sectors. The rose constructed for the main pollutant detected at the CORR site (Zn) is plotted in Figure 9. The main peaks of the rose point to the S, S-SE and E directions, where two iron foundries (A1 and A2) and a wire drawing plant (A3) are located. The highest iron foundry located in the south direction of the sampling site has a capacity of 600 t/year (see A2 in Figure 9).

Finally, approximately 40 % of the metal contribution at the GUAR site was associated with the first factor, with a high contribution from Mn and a relevant concentration of Fe. This can be explained by the proximity of a ferro-manganese alloys plant (see A2 in Figure 10). Iron and Mn were well correlated with PM10, SO_2, NO_x and CO. According to the E-PRTR (Pollutant Release and Transfer Register), these major pollutants are emitted by plant A2 and also by the steel plant located to the N direction (A1 in Figure 10). The profile of the second factor is complex, with intermediate loadings of Cd, Pb, Cu, Ti, Mo, Sb, Fe and Zn. A mixed contribution of traffic and other local industrial sources is assumed. Fe, Zn, Pb and Cd were attributed to the non-integrated steel factory located 4 km to the north of the sampling site (A1), and Cu, Mo and Sb are good tracers of traffic emissions. The highest correlations

between NO_x and the studied elements were obtained for Mo > Cu > Fe. An industrial park located upwind of the receptor point generates substantial traffic from heavy-duty vehicles and may explain the high contribution of this factor (39.8 %). Finally, the last factor is mainly composed of V and Ni and is attributed to liquid fuel combustion. The characteristic wind pattern in the southern portion of Santander Bay is shown in Figure 7(c); the wind rose was calculated at the GUAR site for the period 2008-2009. The predominant wind directions at this site are SW and, to a much lower extent NE, a pattern that has been previously observed (Ruiz et al. 2011): light winds blow predominantly from the SW direction in the fall and winter, whereas moderate onshore breezes from the NE direction are typically observed in the summer. The rose for Mn, the main pollutant at the GUAR site, was plotted on the southern part of the Santander Bay map in Figure 10, together with the rose computed at another site in the bay, Alto Maliaño (ALM). At the ALM site, the Mn peak points to the ferromanganese alloys plant, which agrees with the high contribution of the SW sector observed in Figure 7(c). However, at the GUAR site the highest Mn peak also points to the ferroalloy plant, although the contribution of the NE sector is much lower than that of the SW sector as shown in Figure 7(c). This clearly explains the high contribution of the ferromanganese alloy plant to the levels of Mn in the southern portion of the Santander Bay and explains why the highest levels of Mn are observed at the ALM site, as shown in Table 7.

4. CONCLUSIONS

A study of the metal levels at three receptor points in the Cantabria region (northern Spain), TORR, CORR and GUAR, where local air quality plans had been developed in response to the number of exceedances of the daily PM10 values in the last decade, was presented.

The annual levels of most of the studied elements were lower than those found in other Spanish and European urban/mixed land-use areas. The levels of Zn at the three sites and Mn at the GUAR site were higher than those detected in other urban areas. Such levels of Mn and Zn are only found in urban/industrial mixed land-use areas where iron and steel industries are located.

An inter-site analysis among the three sites, which are relatively close to one another, revealed that although road traffic and residential combustion are common sources of metals, local industrial activities increased the inter-site coefficient of divergence (COD) and

diminished the Pearson inter-site correlation coefficient of the industrial tracers, such as Mn. Moreover, according to the EF analysis, Mn was intermediately enriched at the TORR and CORR sites but highly enriched at the GUAR site, which is located near a ferromanganese plant. The EF analysis also revealed that Fe and V were the least enriched and Zn, Cd, Mo, Pb and Cu were the most enriched elements at the three sites. The models elaborated by the EPA PMF 3.0 software were able to associate more than 89 % of the metals bound to PM10 that were sampled at the studied receptor points. The analysis of the PMF factor profiles, the shapes of the pollutant roses of the main tracers and the previous knowledge of the studied areas were used to identify the main sources of the trace elements at the three sites. At the TORR receptor point, the first factor contributed 55 % of the studied trace element levels, and was mainly attributed to road traffic. The main metal source at the CORR site is an iron foundry and casting industry, with a much higher contribution (73 %) than the other sources. An industrial source (ferromanganese alloys plant) is the most important source at the GUAR site, followed closely by the second factor composed of road traffic and a steel plant.

This study demonstrates the important influence of local industrial sources and road traffic on the levels of trace metals at the studied sites. A reduction of particle emissions from these local sources will decrease the levels of such metals and PM10 and therefore help achieve the goals of the EU Air Quality regulation with respect to PM10.

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Table 1. Number of exceedances of the daily PM10 limit value at the Cantabrian Air Quality Monitoring Network stations

	Year										
	2003[b]		2004[b]		2005[b]	2006[b]	2007[b]	2008[b]	2009[b]	2010[b]	2011[b]
Daily limit value (μg/m³)	**60**	**50[a]**	**55**	**50[a]**	**50**	**50**	**50**	**50**	**50**	**50**	**50**
Station											
Minas	8	18	16	24	38	28	13	11	10	1	10
Zapatón	20	39	29	45	28	16	7	5	3	1	6
Barreda	63	117	63	92	61	92	73	39	36	11	19
Los Corrales de Buelna	61	92	58	75	44	58	45	20	9	11	17
Santander Centro	28	52	24	39	33	28	43	17	13	4	15
Santander Tetuán	31	58	24	37	23	9	27	21	12	1	8
Guarnizo	60	90	52	65	48	29	31	11	8	14	9
Camargo	82	128	88	111	59	61	66	46	25	38	28
Castro Urdiales	49	77	35	50	39	17	7	2	5	16	4
Los Tojos	-	-	-	-	-	-	-	-	-	2	2
Reinosa	28	52	16	22	29	8	6	2	0	6	1

Maximum number of exceedances: 35

(a) Margin of tolerance excluded

(b) Natural events not excluded

Table 2. Element recoveries obtained from SRM1649a, the average of filter blanks and the method detection limits

Element	Recovery (%)	Filter blanks (ng/m^3)	Detection limit (ng/m^3)
As	91[a]	0.05[b]	0.03[b]
Cd	112[a]	0.02[b]	0.01[b]
Ni	115[a]	1.6[b]	0.9[b]
Pb	99[a]	0.5[b]	0.5[b]
Cu	111[a]	1.3[b]	1.1[b]
Cr	68[a]	1.8[b]	2.3[b]
Ti	n.a	0.6[b]	1.2[b]
Mn	96 [a]	1.2[b]	1.1[b]
V	88[a]	0.03[b]	0.05[b]
Mo	n.a	0.3[b]	0.2[b]
Sb	77	0.16	0.02
Fe	75	17.7	4.4
Zn	72	36.6	5.7

[a] Arruti et al., 2010
[b]Arruti et al., 2011a
n.a: certificated value not available for the selected reference material (SRM1649a)

Table 3. Mean (M), standard deviation (s), minimum (Min), maximum (Max) and median (m) of trace metal levels at the TORR site (ng/m^3)

	2008 (N=29)					2009 (N=26)					2010 (N=52)				
	M	**s**	**Min**	**Max**	**m**	**M**	**s**	**Min**	**Max**	**m**	**M**	**s**	**Min**	**Max**	**m**
As	0.18	0.15	<LD	0.72	0.16	0.28	0.2	0.04	0.71	0.23	0.55	0.75	0.03	4.13	0.33
Cd	0.16	0.19	<LD	0.74	0.09	0.16	0.17	0.03	0.83	0.1	0.25	0.52	<LD	3	0.14
Ni	2.81	2.5	<LD	10.4	1.65	4.02	4	0.7	19.4	3.04	3.38	3.7	0.46	19.3	2.11
Pb	12.5	10.7	2.04	44.1	9.1	8.51	7.31	0.91	25.4	4.37	9.24	7.33	0.8	31.8	8.15
Cu	19.3	10.5	<LD	44.8	17.7	18.8	11.4	3.03	56.9	16.7	20.2	11.9	2.92	62.4	17.4
Cr	22.7	58.8	<LD	285	3.45	3.44	3.06	<LD	13.8	1.63	4.86	2	1.83	9.9	4.43
Ti	5.4	8.07	<LD	41.8	3.37	5.38	3.68	0.92	12.9	3.54	6.03	3.97	<LD	19.5	4.91
Mn	22.1	18.4	<LD	76.5	19.7	12.9	9.43	1.87	31.7	10.3	17.5	18.8	1.42	126	12.7
V	1.99	1.41	0.25	5.96	1.69	2.45	1.59	0.32	7.46	2.01	1.75	1.36	<LD	7	1.47
Mo	1.21	0.75	<LD	3.87	0.97	1.35	0.85	0.36	3.27	1.01	1.12	0.79	<LD	3.85	0.89
Sb[a]						1.44	0.66	0.44	2.82	1.36	1.99	1.06	0.27	4.71	2.09
Fe[a]						544	300	113	1,189	514	629	383	79.6	1,770	538
Zn[a]						211	246	<LD	1154	132	354	920	<LD	6326	97.3

[a] Not measured in 2008
LD Limit of detection

Table 4. Mean (M), standard deviation (s), minimum (Min), maximum (Max) and median (m) of trace metal levels at the CORR site (ng/m^3)

	2008 (N=29)					2009 (N=26)					2010 (N=52)				
	M	**s**	**Min**	**Max**	**m**	**M**	**s**	**Min**	**Max**	**m**	**M**	**s**	**Min**	**Max**	**m**
As	0.4	0.43	<LD	2.08	0.29	0.32	0.25	0.08	1.14	0.25	0.4	0.36	<LD	2.43	0.34
Cd	0.26	0.54	<LD	2.75	0.08	0.14	0.1	0.01	0.41	0.11	0.13	0.11	<LD	0.66	0.11
Ni	4.5	9.35	<LD	52.1	2.07	3.27	3.51	0.93	18.8	2.27	3.48	3.25	0.68	20.3	2.48
Pb	18.8	21.5	3.25	112	11.8	12.3	11.4	1.7	45.4	7.3	12.1	13.3	0.92	92.5	9.21
Cu	7.32	6.87	<LD	28.5	4.98	6.52	4.99	1.75	23.4	4.8	7.66	5.54	1.37	32	6.31
Cr	7.38	8.8	<LD	34.8	2.87	<LD	1.18	<LD	5.03	<LD	4.87	3.25	1.63	19.4	4.09
Ti	8.1	11.1	<LD	46.9	5.7	5.82	2.52	1.14	10.4	5.64	6.04	4.52	0.84	31	5.23
Mn	32.1	28.8	<LD	134	25	20	14.5	2.64	50.6	14.6	22.3	17.8	<LD	91	17.1
V	1.53	1.51	<LD	6.28	1.07	2.1	1.34	0.47	5.45	1.73	1.35	0.84	0.19	3.33	1.16
Mo	0.82	0.86	<LD	3.41	0.51	0.88	0.8	<LD	3.26	0.54	0.43	0.36	0.06	1.45	0.38
Sb[a]						0.5	0.36	0.05	1.84	0.41	0.63	0.42	0.09	2.26	0.52
Fe[a]						540	439	<LD	1,452	393	562	462	5.66	2,275	476
Zn[a]						188	159	8.38	574	112	219	183	<LD	915	188

[a] Not measured in 2008
LD Limit of detection

Table 5. Mean (M), standard deviation (s), minimum (Min), maximum (Max) and median (m) of trace metal levels at the GUAR site (ng/m^3)

	2008 (N=28)					2009 (N=28)				
	M	**s**	**Min**	**Max**	**m**	**M**	**s**	**Min**	**Max**	**m**
As	0.09	0.12	<LD	0.49	0.04	0.22	0.17	0.04	0.73	0.17
Cd	0.12	0.13	<LD	0.51	0.08	0.24	0.26	0.02	0.97	0.13
Ni	4.24	3.32	<LD	14.6	3.38	4.39	4.75	0.87	21.1	2.72
Pb	12.1	11.1	1.73	57.4	8.59	8.99	8.9	0.55	37.3	6.72
Cu	7.38	6.17	<LD	28.8	5.44	11.4	11	0.86	48.3	8.07
Cr	8.97	5.36	<LD	22.4	7.87	3.75	3.5	<LD	13.9	<LD
Ti	5.18	3.9	<LD	23.3	4.78	4.91	3.36	0.6	13.6	4.05
Mn	160	159	6.51	515	82	118	169	1.98	587	35.6
V	2.16	1.62	0.2	7.21	1.66	2.39	1.59	0.46	5.83	2.16
Mo	0.37	0.28	<LD	1.01	0.24	0.66	0.69	<LD	2.83	0.42
Sb[a]						0.82	0.71	<LD	2.37	0.58
Fe[a]						426	344	<LD	1,436	353
Zn[a]						85.4	104	9.73	531	60.1

[a] Not measured in 2008
LD Limit of detection

Table 6. Target/limit/guideline values of metals (ng/m^3)

Element	EU target/limit value	WHO guideline value	Averaging time
As	6	-	Annual
Cd	5	5	Annual
Pb	500	500	Annual
Mn	-	150	Annual
Ni	20	-	Annual
V	-	1000	24 hours

Table 7. Summary of the mean metal concentrations (ng/m^3) detected in different Spanish and European urban and urban/industrial areas

	Type	As	Cd	Ni	Pb	Cu	Cr	Ti	Mn	V	Mo	Sb	Fe	Zn
CANTABRIA														
Los Corrales de Buelna[a]	U/I	0.38	0.17	3.7	14	7.29	5.08	6.55	25.2	1.58	0.65	0.59	574	226
Barreda[a]	T/I	1.11	0.2	3.37	10	19.6	9.48	5.7	17.6	1.98	1.2	1.81	601	306
Guarnizo[a]	I	0.16	0.18	4.32	10.5	9.38	6.91	5.05	139	2.28	0.51	0.82	426	85.4
Alto Maliaño[b]	I	0.63	0.81	5.01	28.6	10	3.09	-	1,071	1.85	1.2	1.34	477	341
Santander[c]	U	0.4	0.3	1.2	6.5	4.8	5	2.5	41.1	1.2	0.4	-	-	-
Torrelavega[d]	U/I	0.6	0.3	1.5	19.9	46.9	3.8	15.8	28.7	2.6	3.2	2.7	400	148
SPAIN														
Llodio[e]	I	1.8	1.2	33	102	32.6	24.6	24.2	86.5	8.3	15.5	3.6	-	417
Tarragona[e]	U/I	0.8	0.3	4.2	25.5	32.9	2.9	22.5	9.2	7.7	2.2	6.9	-	35
Zaragoza[f]	U	-	-	0.8	18.7	22.8	7.7	-	24.7	6.6	-	-	666	212
Huelva[g]	I	6.2	0.7	3.7	14.4	45.3	2.3	46.5	9.6	5.3	12.2	1.6	600	47.4
Spanish range[h]	*U*	*0.3-1.6*	*0.1-0.7*	*2-7*	*7-57*	*7-88*	*2-8*	*18-83*	*4-23*	*2-15*	*2-5*	*1-11*	*-*	*14-140*
EUROPE														
Palermo (Italy)[i]	T	1.4	-	8	17	83	9.3	-	18	22	7	19	827	60
Dunkerque (France)[j]	I	2.49	1.27	9.43	34	15.6	4.99	17	99	16	2.14	2.15	1,752	131
Athens (Greece)[k]	I	6.1	3.7	15.9	71.1	43.2	14.5	-	21.1	8.6	-	-	-	-
Lisbon (Portugal)[l]	U	0.47	-	4.2	14.6	11.1	-	29.5	6.5	11.2	-	2.6	400	36
Dundee (UK)[m]	U	-	-	25	21	24	-	-	-	-	-	-	-	28
Rome (Italy)[n]	U	2.28	-	-	-	85.3	-	177	57.1	27.7	-	7.01	-	-

U: urban; I: industrial; T: traffic

[a]Present study; [b]CIMA (2010); [c]Arruti et al. (2011a); [d]Moreno et al (2011); [e]Moreno et al. (2006); [f]López et al. (2005); [g]Fernández-Camacho et al. (2012); [h]Querol et al. (2007); [i]Dongarrà et al. (2007); [j]Gaudry et al. (2008); [k]Manalis et al. (2005); [l]Almeida et al. (2013); [m]Qin and Oduyemi (2003); [n]Avino et al. (2014)

Table 8. Coefficient of Divergence (COD) between the TORR, GUAR and CORR sites

	2008	2009	2010
$COD_{CORR\text{-}TORR}$	0.30	0.22	0.26
$COD_{CORR\text{-}GUAR}$	0.35	0.27	-
$COD_{TORR\text{-}GUAR}$	0.37	0.30	-

Table 9. Inter-site Pearson correlation coefficients for the studied elements between the TORR, GUAR and CORR sites

	CORR-TORR	TORR-GUAR	CORR-GUAR
As	0.60	0.64	0.40
Cd	0.45	0.59	0.17
Ni	-0.18	-0.02	-0.26
Pb	0.64	0.01	-0.08
Cu	0.49	-0.10	0.43
Cr	0.004	0.37	0.08
Ti	0.73	0.68	0.81
Mn	0.73	0.24	0.12
V	0.69	0.84	0.73
Mo	0.79	0.52	0.73
Sb	0.23	0.05	0.79
Fe	0.52	0.24	0.10
Zn	0.55	0.79	0.43

Table 10. Contribution of each factor at the studied sites

Site	Factor 1 (%)	Factor 2 (%)	Factor 3 (%)
TORR	55.3	25.2	19.5
CORR	73.0	16.5	10.5
GUAR	40.1	39.8	20.1

FIGURE CAPTIONS

Figure 1. Location of the sampling sites

Figure 2. Comparison between the annual mean levels of the studied elements and the range typically detected in Spanish urban and urban-mixed land-use areas[1]: (a) TORR; (b) CORR; (c) GUAR

[1] Range in Spanish urban areas obtained from Querol et al. (2007)

Figure 3. Enrichment factors of the studied elements: (a) 2008; (b) 2009; (c) 2010

Figure 4. Factor profiles obtained from PMF at the TORR site

Figure 5. Factor profiles obtained from PMF at the CORR site

Figure 6. Factor profiles obtained from PMF at the GUAR site

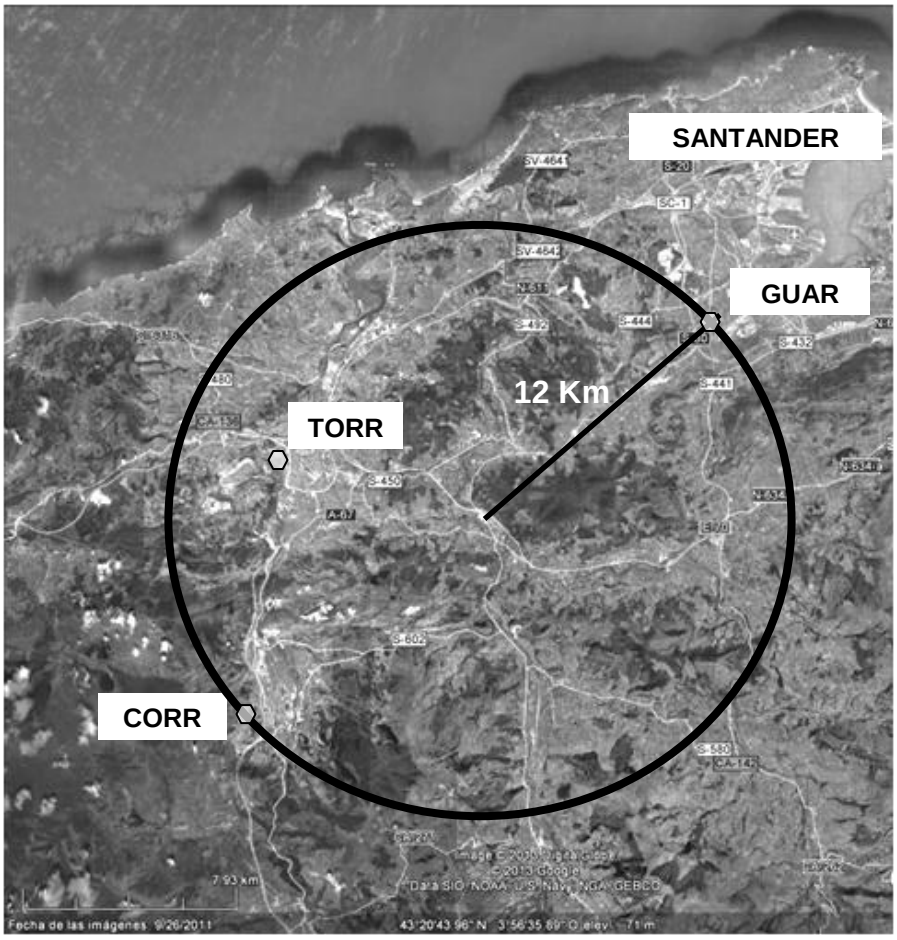
Figure 7. Wind roses calculated for the studied sites: (a) TORR (2008-2010); (b) CORR (2008-2010); (c) GUAR (2008-2009)

Figure 8. Copper rose (ng/m^3) at the TORR site

Figure 9. Zinc rose (ng/m^3) at the CORR site

Figure 10. Manganese rose (ng/m^3) in Camargo: GUAR and ALM sites

FIGURES



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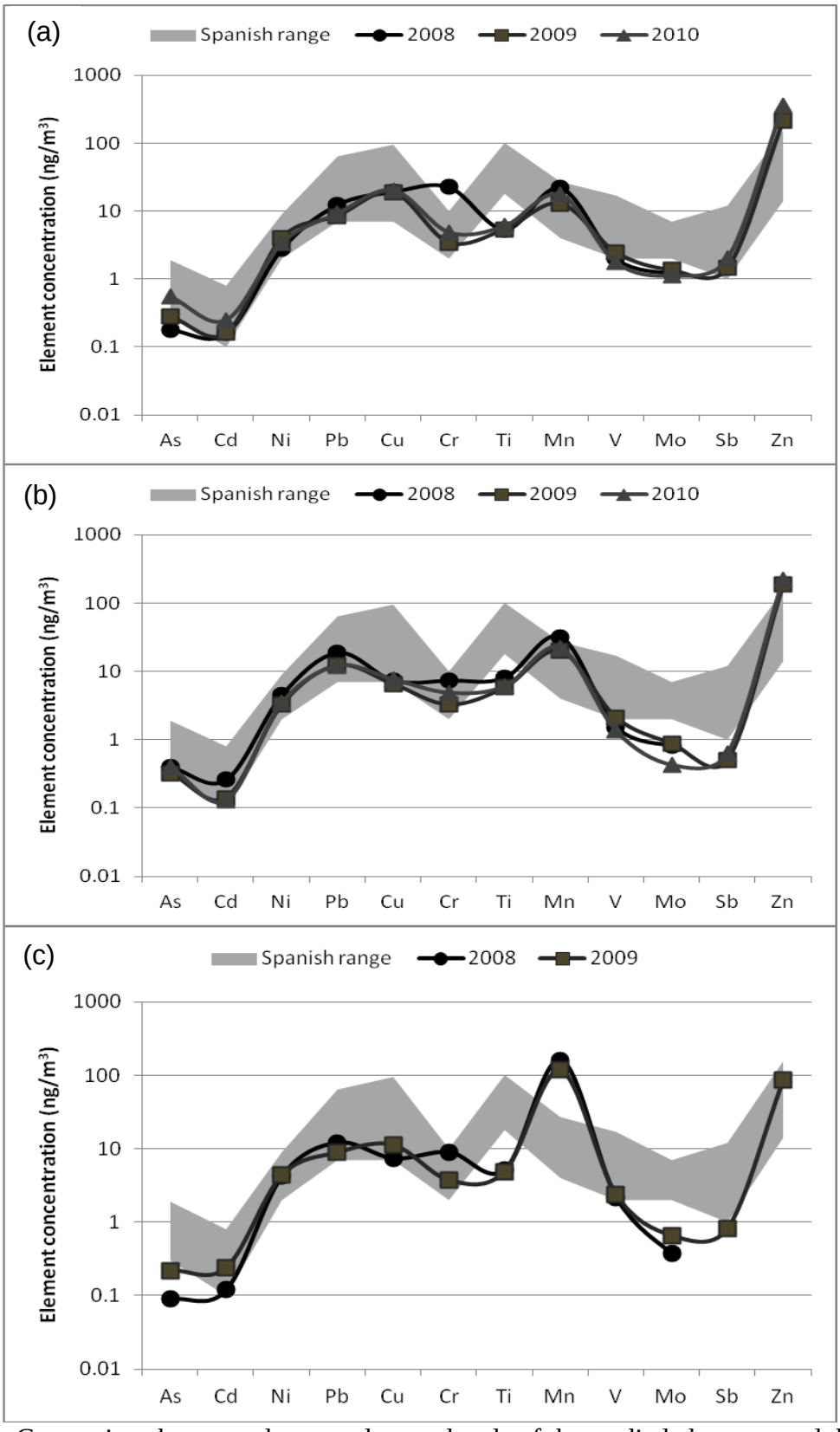

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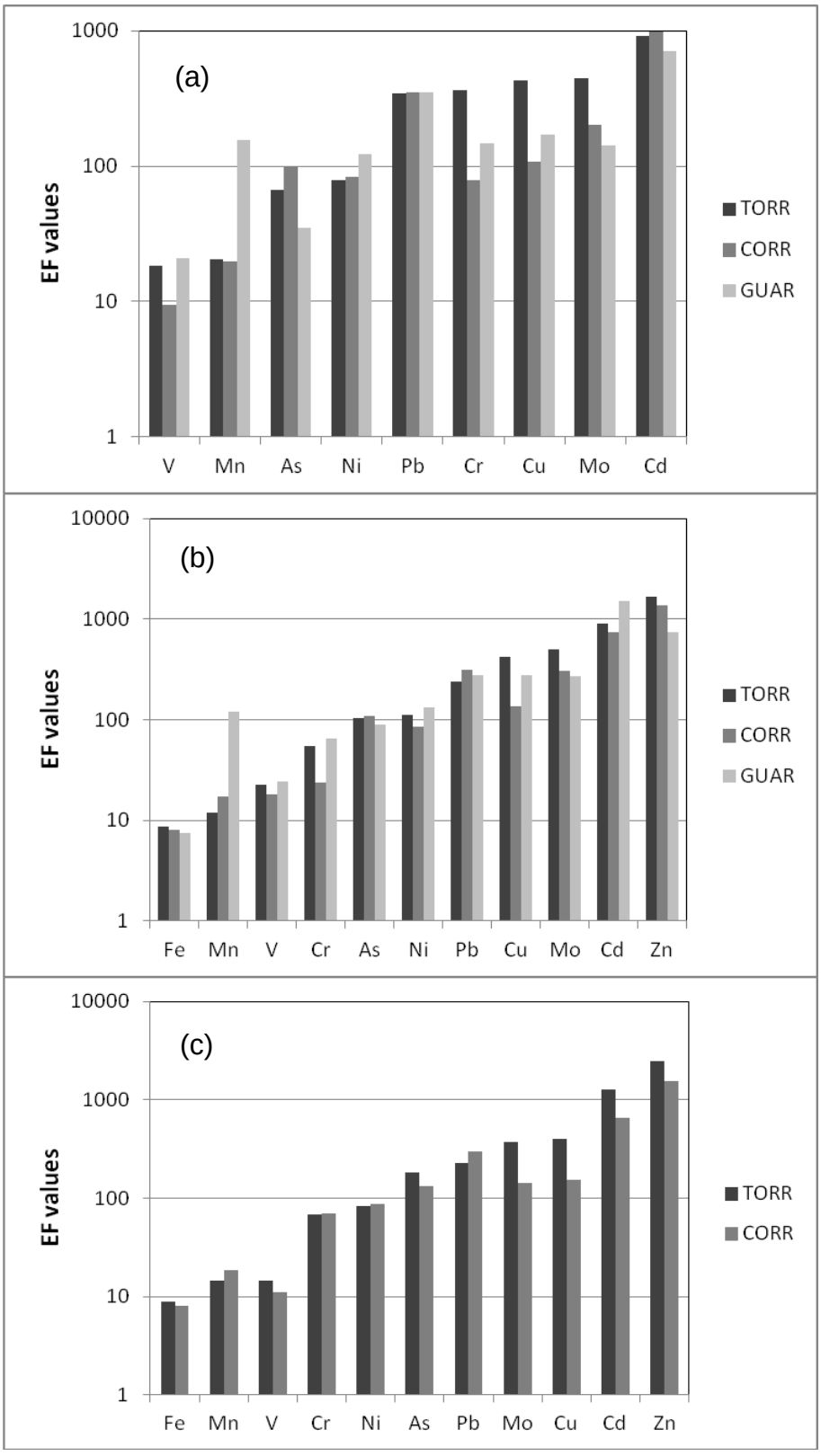

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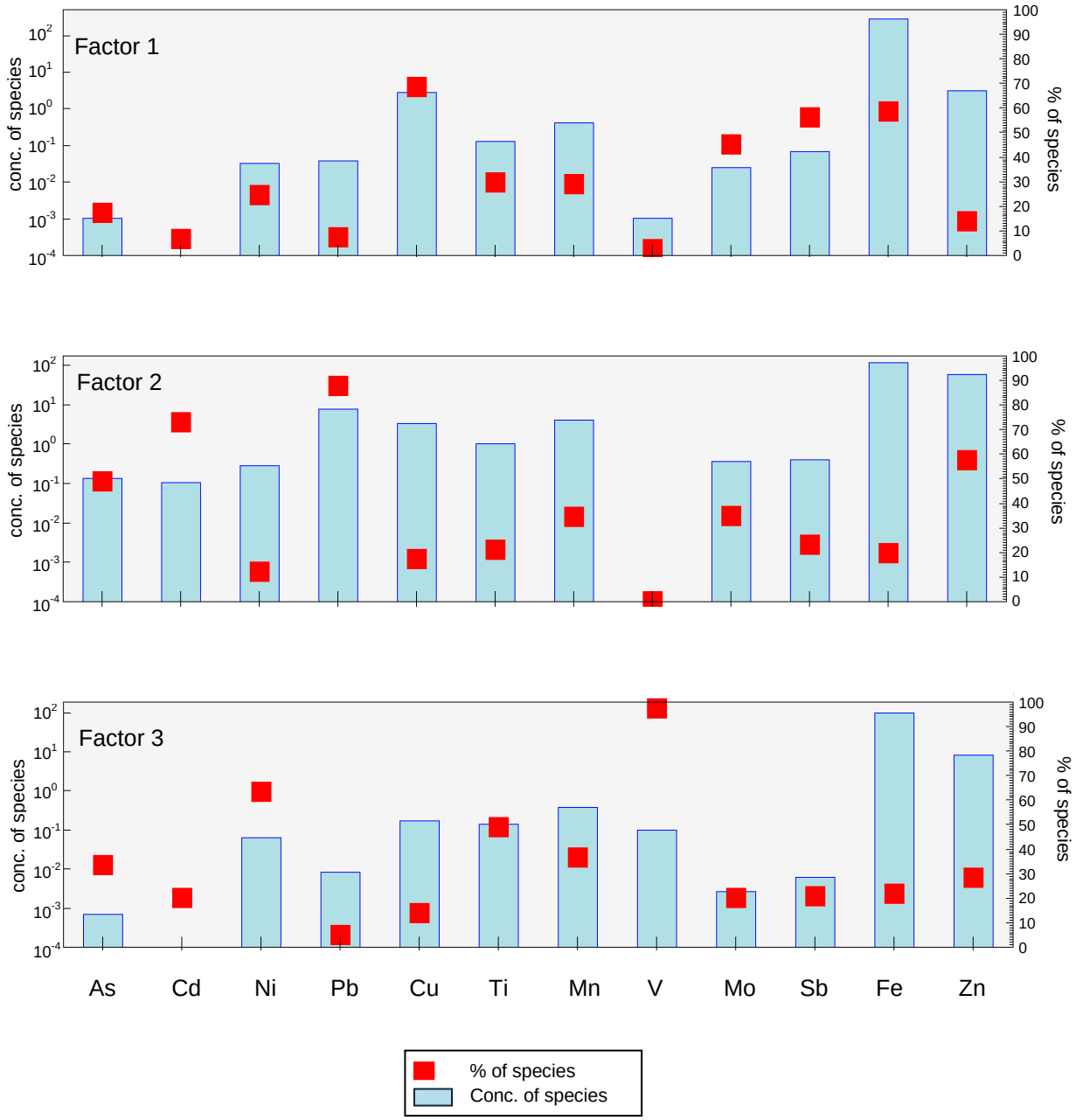

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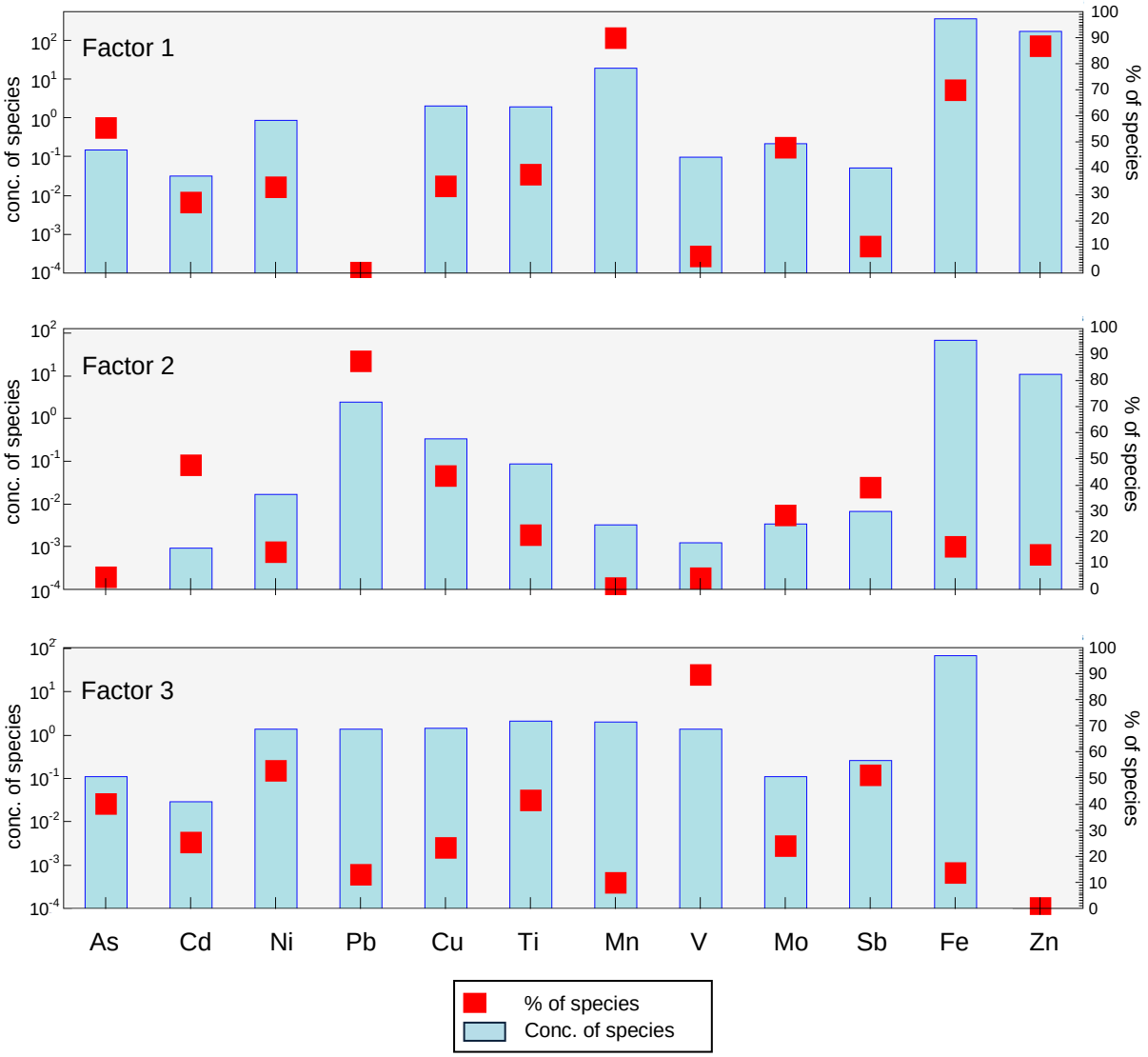

Figure 5. Factor profiles obtained from PMF at the CORR site

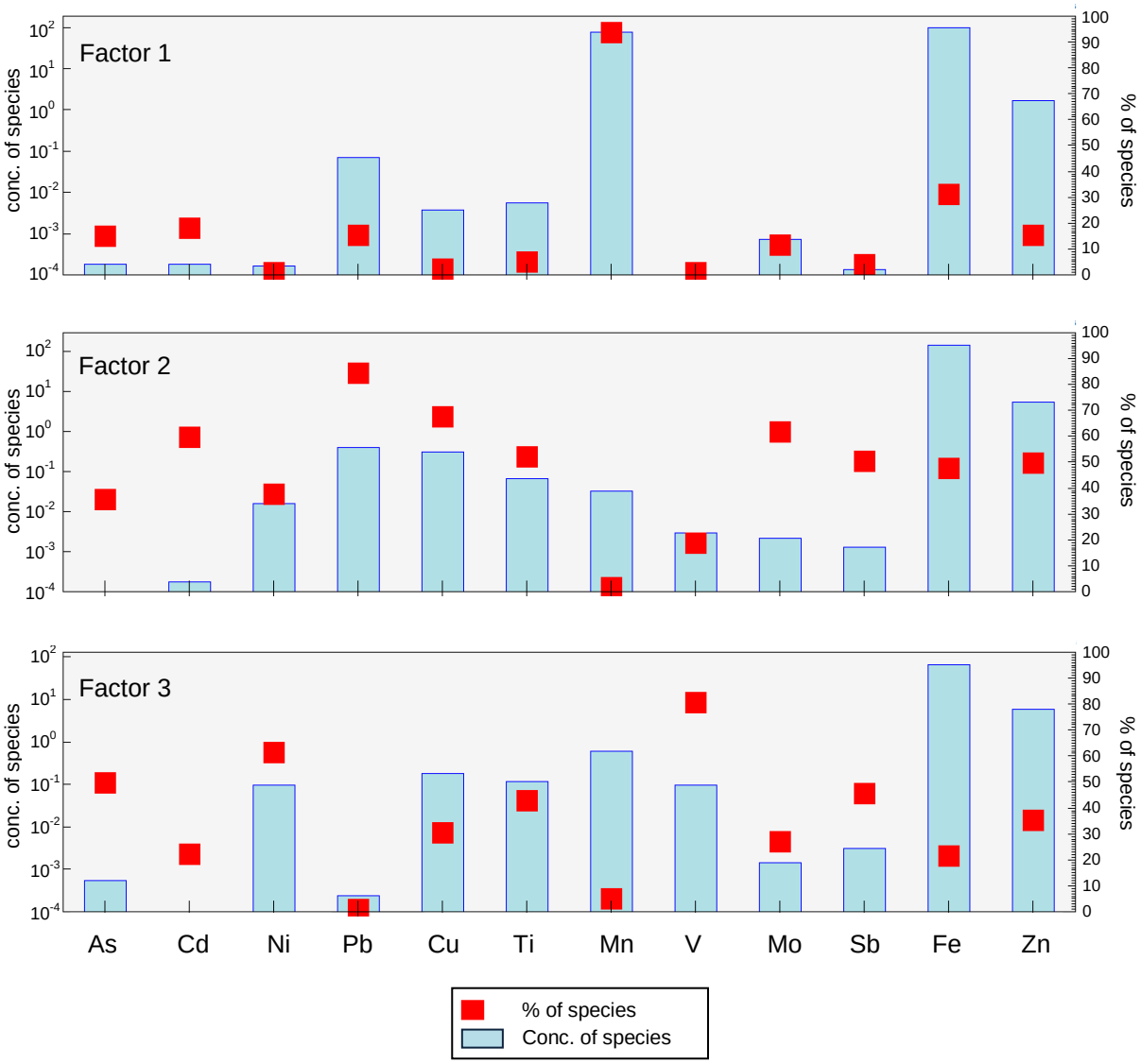

Figure 6. Factor profiles obtained from PMF at the GUAR site

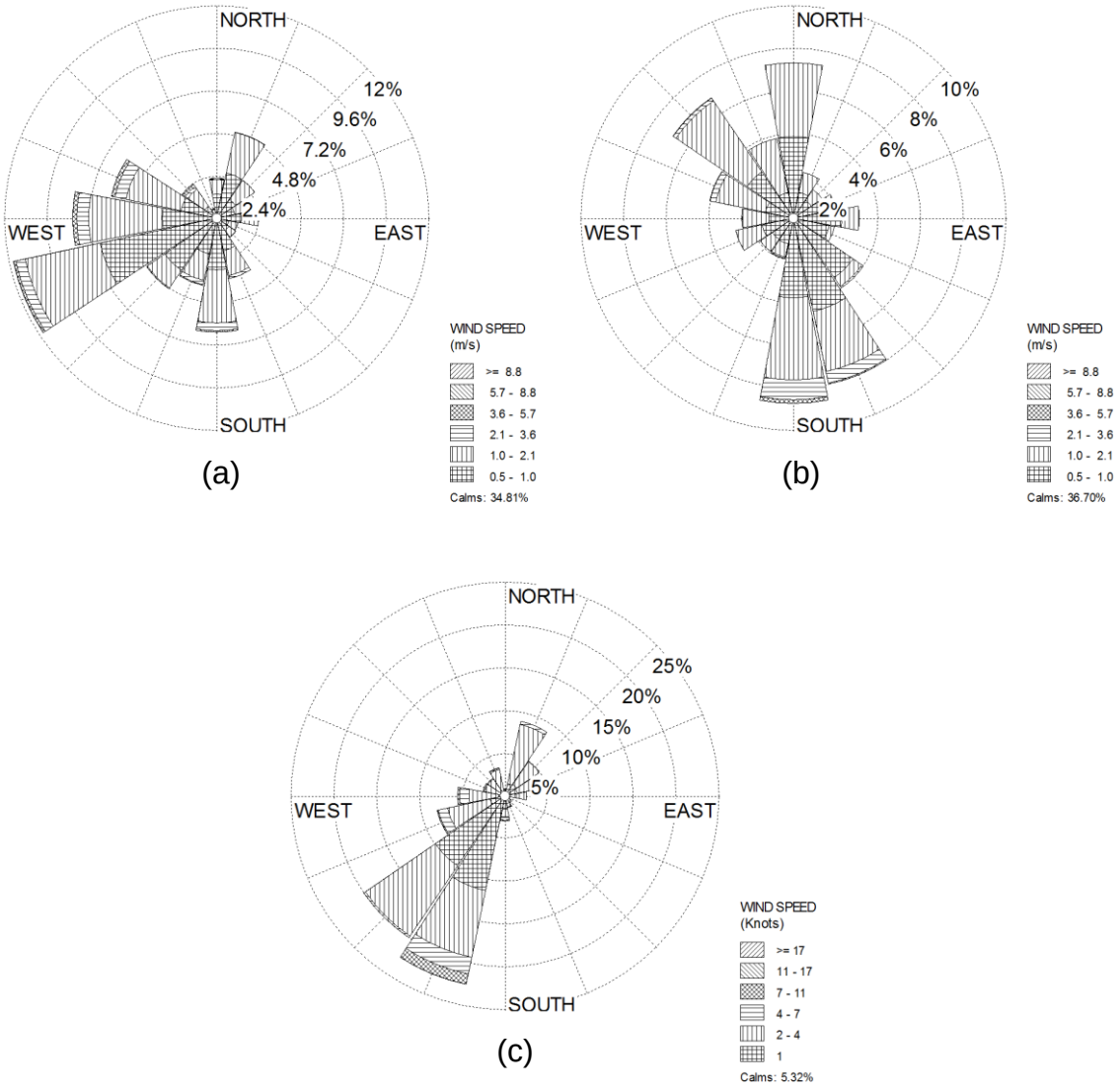

Figure 7. Wind roses calculated for the studied sites: (a) TORR (2008-2010); (b) CORR (2008-2010); (c) GUAR (2008-2009)

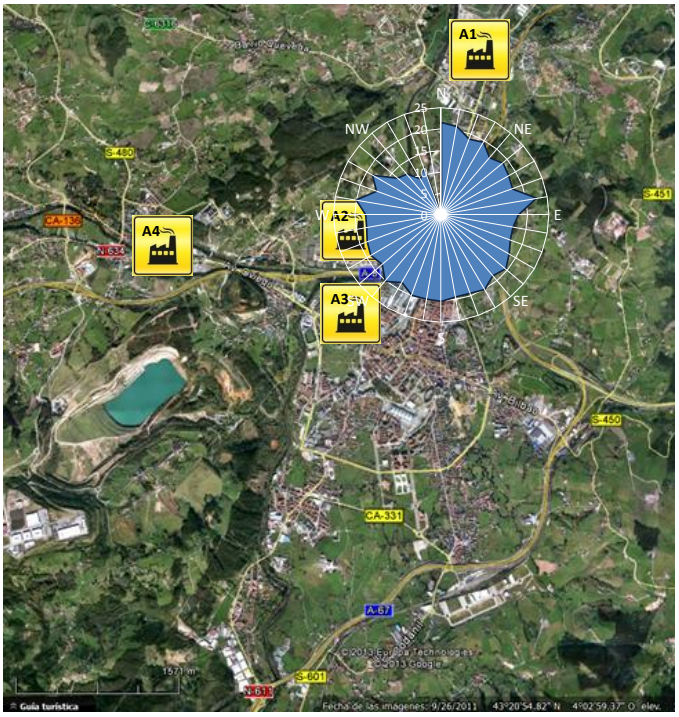

Figure 8. Copper rose (ng/m^3) at the TORR site

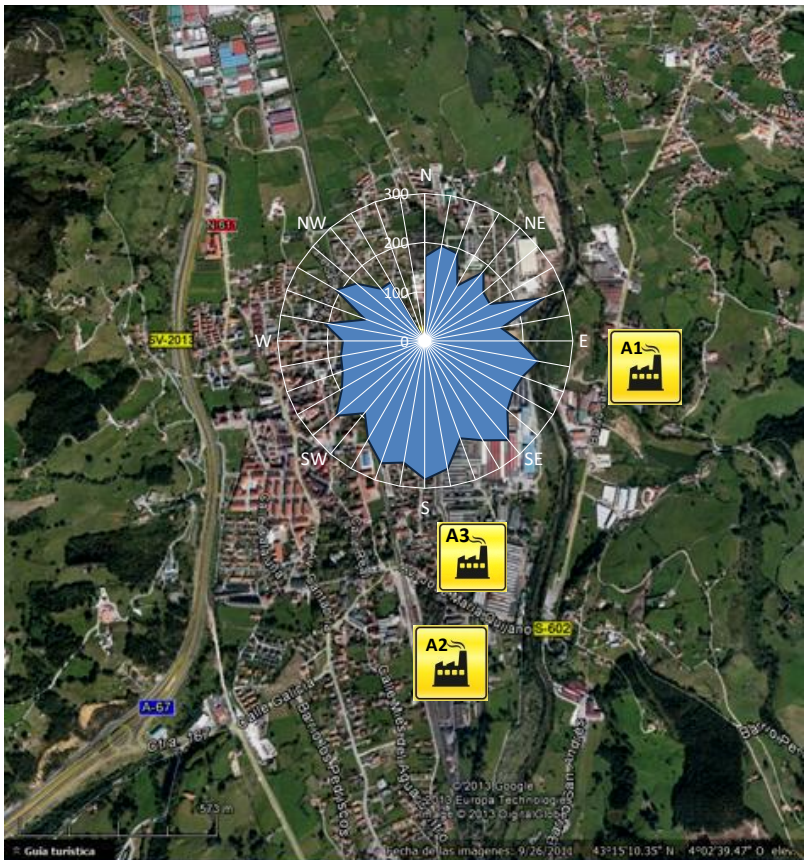

Figure 9. Zinc rose (ng/m^3) at the CORR site

Figure 10. Manganese rose (ng/m^3) in Camargo: GUAR and ALM sites